

Surface vs. bulk Coulomb correlations in photoemission spectra of perovskites

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Recent photoemission spectra of the perovskite series $\text{Sr}_x\text{Ca}_{1-x}\text{VO}_3$ revealed strong modifications associated with surface contributions. To study the effect of Coulomb correlations in the bulk and at the surface the quasi-particle spectra are evaluated using the dynamical mean field theory. It is shown that as a result of the reduced coordination number of surface atoms correlation effects are stronger at the surface than in the bulk, in agreement with experiment.

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Photoemission is a key spectroscopy for the investigation of electronic properties of strongly correlated materials. Because of its surface sensitivity there is growing concern to what extent the data are representative of bulk properties and whether they need to be corrected for surface effects influencing the one- and many-electron properties. To study these questions Maiti *et al.* [1] and Sekiyama *et al.* [2] performed photoemission measurements on $\text{Sr}_x\text{Ca}_{1-x}\text{VO}_3$ using a wide range of photon energies. As a result of the frequency dependent escape depth of the photoelectron, the spectra reveal striking variations evidently associated with surface modifications of the electronic structure: emission from the coherent peak near the Fermi level is reduced and correlation-induced satellites have larger weight than in the bulk. The same trend is observed on SrRuO_3 [3]. Another example is Sr_2RuO_4 for which earlier photoemission data appeared to be in conflict with de Haas-van Alphen measurements [4]. Recent experimental and theoretical work proved that this discrepancy can be resolved by accounting for the surface reconstruction of Sr_2RuO_4 which leads to significant changes in photoemission spectra [5].

The understanding of surface effects in photoemission spectra of transition metal oxides is important in order to distinguish them from correlation phenomena in the bulk. Although the electronic properties of strongly correlated materials are currently a field of intense experimental and theoretical investigation [6, 7, 8] surface effects have so far received little attention [9]. For this purpose photoemission studies of the series $\text{Sr}_x\text{Ca}_{1-x}\text{VO}_3$ [1, 2, 10, 11, 12] are very useful since the one-electron properties are relatively simple and the ratio U/W can be tuned systematically. Here, U is the on-site Coulomb energy and W the width of the relevant bands near the Fermi level. While SrVO_3 is considered to be a moderately correlated metal with a clear quasi-particle peak near E_F , the slightly smaller band width of CaVO_3 is believed to push this system closer to the metal-insulator transition. For this reason CaVO_3 has become a key system of investigation [13, 14, 15]. For instance, recent de Haas-van Alphen measurements on CaVO_3 [15] detected a cubic Fermi surface although this system exhibits orthorhombic distortions.

In the present work we use the dynamical mean field

theory (DMFT) [7, 16, 17] to evaluate the surface and bulk quasi-particle spectra of SrVO_3 . We show that because of the planar electronic structure of perovskite systems and the concomitant narrowing of the surface local density of states correlation effects at the surface are more pronounced than in the bulk. In the perovskites this enhancement is particularly strong since the local Coulomb energy is not far from the critical value for a metal-insulator transition. Such a trend had been predicted by Potthoff and Nolting [9] who studied the metal-insulator phase diagram for a semi-infinite simple cubic s band at half filling. Here we calculate the self-energy for a multi-band system using a realistic local density of states appropriate for SrVO_3 and find qualitative agreement with photoemission data [1, 2].

Electronic structure calculations for SrVO_3 within the local density approximation (LDA) [18] show that the conduction bands near E_F consist of degenerate t_{2g} bands derived from V^{4+} ($3d^1$) ions. The filled O 2p bands are separated from the t_{2g} levels by a gap of about 1 eV, and the cubic crystal field of the V-O octahedron shifts the e_g bands above the t_{2g} bands. The t_{2g} bands can be represented via a tight-binding Hamiltonian with diagonal elements $h_{xy,xy}(k) = e_d + t_0(c_x + c_y) + t_1c_xc_y + [t_2 + t_3(c_x + c_y) + t_4c_xc_y]c_z$, where $c_i = 2\cos(k_ia)$, $i = x, y, z$ and a is the lattice constant. Cyclic permutations yield $h_{xz,xz}(k)$ and $h_{yz,yz}(k)$. The t_i denote effective hopping integrals representing the V-O-V hybridization, where $t_{0,2}$, $t_{1,3}$, and t_4 specify the interaction between first, second and third neighbors, respectively. For symmetry reasons off-diagonal elements arise only between second and third nearest neighbors and are of the form $h_{xy,xz}(k) = -t'_{1,2}s_ys_z - t'_2c_xs_ys_z$, where $s_i = 2\sin(k_ia)$, i.e., they vanish at high-symmetry points. Since the $t'_{1,2}$ are very small we neglect the off-diagonal elements so that the energy bands are given by $\epsilon_i(k) = h_{i,i}(k)$, with $i = xy, xz, yz$. The parameters e_d and $t_0 \dots t_4$ can be found by fitting the LDA energies at high-symmetry points of the Brillouin Zone.

Fig. 1 (a) shows the t_{2g} bulk bands of SrVO_3 . According to the predominantly planar electronic structure, the bulk density of states $\rho_b(\omega)$ exhibits the characteristic asymmetric peak related to the van Hove singularity at the X point (see Fig. 1 (b)). The overall shape of the bulk

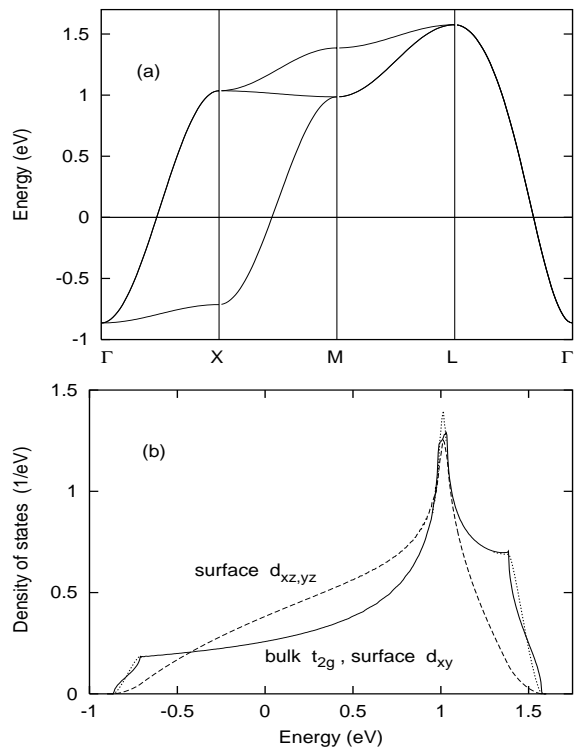


FIG. 1: (a) Tight-binding fit to LDA t_{2g} bulk bands of SrVO_3 ($E_F = 0$). (b) Solid curve: isotropic bulk density of states; dashed and dotted curves: local density of $d_{xz,yz}$ and d_{xy} states in the first layer of SrVO_3 .

density of states agrees with LDA calculations [18]. At the surface, the t_{2g} degeneracy is lifted since only the d_{xy} band exhibits strong dispersion within the surface plane (the z axis defines the surface normal). To evaluate the surface density of states we use a Green's function formalism [19] for semi-infinite tight-binding systems. As electronic structure calculations for SrVO_3 surfaces are not available, we assume the tight-binding parameters to coincide with those in the bulk, except for a small surface potential to ensure charge neutrality.

Fig. 1 (b) shows the local density of states $\rho_s(\omega)$ of the $d_{xz,yz}$ bands for the surface layer of SrVO_3 . Its spectral weight is reduced at low and high energies but enhanced at intermediate energies. Thus, the effective width of $\rho_s(\omega)$ is smaller than that of $\rho_b(\omega)$ although their total widths are identical. In contrast to the $d_{xz,yz}$ density, the density of d_{xy} states nearly coincides with the bulk density, reflecting the planar nature of the t_{2g} states. In the deeper layers the local density of $d_{xz,yz}$ states approaches $\rho_b(\omega)$ rather quickly, the main effect consisting in an oscillatory distortion of the spectral shape. This rapid convergence is a consequence of the tight-binding character of the t_{2g} bands. It would be desirable to carry out self-consistent electronic structure calculations for SrVO_3 surfaces since they should provide a more accurate density of states. Nevertheless, the key effect discussed here, namely, the preferential narrowing of the local density of

$d_{xz,yz}$ states, should hold quite generally.

To interpret the experimental photoemission data we evaluate the quasi-particle spectra by accounting for local Coulomb correlations. According to the one-electron properties discussed above we are dealing with a non-isotropic system where two narrow bands interact with a wider band. In the first layer this difference in effective band width is largest and it diminishes rapidly towards the interior of the system. This situation is reminiscent of the layer perovskite Sr_2RuO_4 , which essentially consists of Ru sheets containing two narrow $d_{xz,yz}$ bands interacting with a wide intra-planar d_{xy} band. The peculiar feature of this system is the fact the on-site Coulomb energy lies between the single-particle widths of the non-degenerate t_{2g} bands: $W_{xz,yz} < U < W_{xy}$ [20]. In the present case the difference between $d_{xz,yz}$ and d_{xy} bands at the surface is less pronounced so that $W_i < U$ for all three bands. Nevertheless, since in the first layer the effective width of $d_{xz,yz}$ states is reduced, the influence of Coulomb correlations on the surface bands should be stronger than on the wider bulk bands.

The key quantity characterizing the effect of Coulomb correlations is the complex self-energy. Since we neglect the weak hybridization between t_{2g} bands, $\Sigma(\omega)$ is diagonal in orbital space. Despite this simplification, a full description of correlations near the surface would be exceedingly complicated since, in principle, it would require a mixed momentum/real space approach in order to handle the loss of translational symmetry normal to the surface. This could be accomplished using a cluster formalism where the semi-infinite system is represented via a slab of finite thickness. Unfortunately, the planar character of t_{2g} orbitals leads to a slowly convergent local density of $d_{xz,yz}$ states, with many spurious $1/\sqrt{\omega}$ van Hove singularities stemming from the quasi-one-dimensional hopping parallel to the surface. On the other hand, a cluster generalization of the DMFT is feasible today only for very small cluster size. We therefore ignore the momentum variation of the self-energy and assume that, for a given layer, it depends only on the local density of states within that layer [9]. The reduced dimensionality at the surface enters the many-body calculation via the layer-dependent density of states. In view of the local Coulomb interaction this assumption seems justified for qualitative purposes.

Before discussing the quasi-particle spectra derived within the DMFT it is useful to compare the frequency dependence of the self-energy in the bulk and at the surface. For convenience we give here the results obtained within non-self-consistent second-order perturbation theory since this provides a clear identification of the various orbital contributions to the diagonal elements $\Sigma_i(\omega)$ [20]. Fig. 2 illustrates the second-order self-energy for $U = 4.3$ eV and $J = 0.7$ eV. Although the total widths of the bulk and surface densities shown in Fig. 1 are the same, the effective band narrowing at the surface yields a correspondingly narrower distribution of $\text{Im}\Sigma_{xz,yz}(\omega)$ compared to $\text{Im}\Sigma_b(\omega)$ for the isotropic bulk. Because

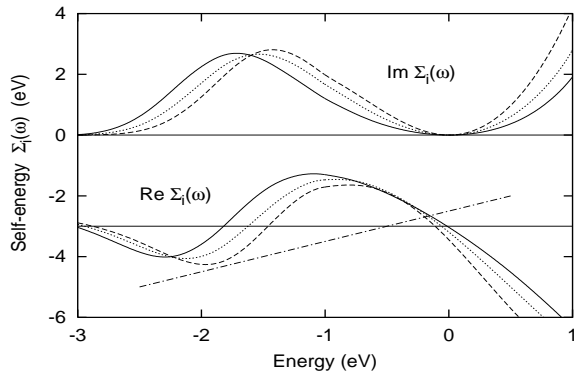


FIG. 2: Second-order self-energy of SrVO_3 . Solid curves: bulk t_{2g} self-energy; dashed (dotted) curves: $d_{xz,yz}$ (d_{xy}) self-energy for surface layer. For clarity the real part is shifted down by 3 eV. The straight line gives $\omega - \epsilon_k$ for $\epsilon_k = -0.5$ eV.

of the orbital mixing via the on-site Coulomb interaction $\text{Im} \Sigma_{xy}(\omega)$ lies between these two distributions. From the Kramers-Kronig relations it then follows that $\text{Re} \Sigma_{xz,yz}(\omega)$ exhibits a more pronounced minimum below the band bottom than $\text{Re} \Sigma_b(\omega)$. Thus, as indicated by the line $\omega - \epsilon_k$ for a typical band energy ϵ_k , the surface satellite appears at a lower value of U than in the bulk. Analogous arguments hold for the upper Hubbard peak. This qualitative picture is fully supported by the more accurate DMFT results discussed below.

In the DMFT the self-energy elements $\Sigma_i(\omega)$ are functionals of the bath Green's functions $\mathcal{G}_i^{-1} = G_i^{-1} + \Sigma_i$. The quasi-particle densities of states are related to the local G_i via $N_i(\omega) = -\text{Im} G_i(\omega)/\pi$. On-site Coulomb correlations are treated using the self-consistent multi-band Quantum Monte Carlo method (for a review, see Ref. [7]). The temperature of the simulation is 12.5 meV with 64 imaginary time slices and several runs using 10^5 Monte Carlo sweeps. The quasi-particle density of states is obtained via maximum entropy reconstruction [21].

Fig. 3(a) shows the bulk quasi-particle density of states of SrVO_3 for two Coulomb energies: $U = 4.0$ eV and 4.3 eV. The exchange energy is $J = 0.7$ eV [22]. These results show that in the bulk U must be larger than 4 eV to obtain the satellite observed in photoemission spectra [1, 2]. The peak near 2 eV above E_F agrees with inverse photoemission data [11]. Although for $U = 4$ eV there is considerable correlation-induced band narrowing and an emerging satellite shoulder, the increase of U to 4.3 eV yields an even narrower coherent feature near E_F , with the missing weight shifted to the lower and upper Hubbard bands. Note that $N_b(E_F) = \rho_b(E_F)$ which follows from the local approximation implicit in the DMFT for isotropic systems [23]. The most recent photoemission data [2] confirm this result. The spectra shown in Fig. 3(a) qualitatively agree with DMFT-LDA results for the $3d^1$ perovskite $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ [24] which exhibits a similar t_{2g} bulk density of states.

The surface quasi-particle spectra for SrVO_3 are shown in Fig. 3(b) and (c). The lower Hubbard peak of the

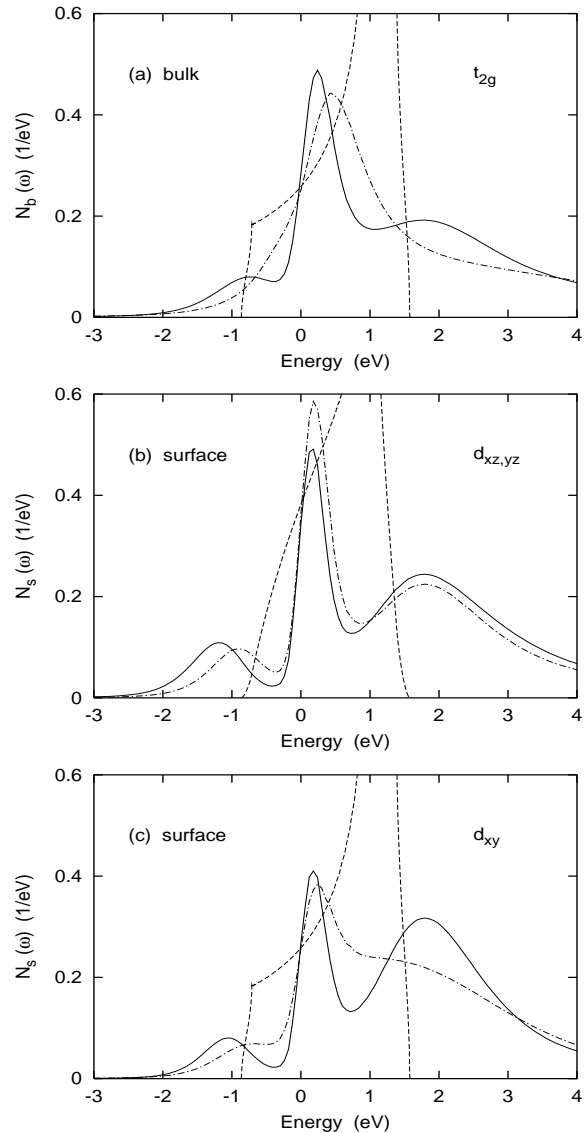


FIG. 3: Quasi-particle density of states of SrVO_3 derived from DMFT. (a) bulk t_{2g} states, (b) surface $d_{xz,yz}$ states, (c) surface d_{xy} states. Solid curves: $U = 4.3$ eV; dot-dashed curves: $U = 4.0$ eV; dashed curves: bare densities.

$d_{xz,yz}$ states is clearly visible already for $U = 4$ eV because of the narrower local density of states in the first layer. A larger U shifts the satellite to higher binding energies. The comparison with the spectra shown in Fig. 3(a) demonstrates that correlation effects for a fixed value of U are stronger at the surface than in the bulk: The coherent peak near E_F is narrower at the surface and the incoherent satellite feature is more pronounced than in the bulk, in agreement with experiment [1, 2, 3].

The surface quasi-particle density of d_{xy} states in Fig. 3(c) is intermediate between $N_b(\omega)$ and $N_s(\omega)$ for $d_{xz,yz}$. Although there is little single-electron hybridization between t_{2g} bands, the local Coulomb interaction mixes them so that the d_{xy} surface spectrum involves contributions arising from the more strongly correlated

$d_{xz,yz}$ states. Another consequence of the anisotropic surface self-energy is the correlation-induced charge transfer between subbands [20]. Here, we find that 0.06 electrons are shifted from the d_{xy} to the $d_{xz,yz}$ bands. Also, the quasi-particle partial densities of states at E_F do not need to coincide with the bare partial densities. The coupling between narrow and wide bands is a genuine multi-band effect and underlines the fact that single-particle bands in the presence of local Coulomb interactions cannot be considered independently. This issue will be considered in more detail elsewhere [26].

Note that the many-body reduction of the quasi-particle band width is much larger than the surface-induced one-electron band narrowing. On the other hand, since with $U/W \approx 2$ the on-site Coulomb energy is not far from the critical value for a metal-insulator transition [7], the band narrowing substantially enhances the influence of correlations at the surface.

It would be interesting to perform angle-resolved photoemission measurements to determine the correlation-induced band narrowing of the SrVO_3 t_{2g} bands. For instance the energy at $\bar{\Gamma}$ should be only a few tenths of an eV below E_F instead of 1 eV as predicted by the LDA. Accordingly, the true t_{2g} bands should be considerably flatter than the single-particle bands. Also, measurements using polarized light could help to separate correlation effects in the d_{xy} and $d_{xz,yz}$ bands.

We finally comment on the difference between CaVO_3 and SrVO_3 . According to LDA band structure calculations for CaRuO_3 and SrRuO_3 [25], orthorhombic dis-

tortions cause a slight narrowing of the t_{2g} bands and a strong broadening of the van Hove singularity above E_F . Assuming the same on-site Coulomb energy for the V^{4+} ions in CaVO_3 and SrVO_3 , a smaller bulk band width of CaVO_3 implies a transfer of spectral weight from the coherent to the incoherent peak. At present, the available data [1, 2, 10, 11, 12] do not yet fully agree on the magnitude of this effect. At the surface, such a transfer of spectral weight should be more pronounced because of the band narrowing discussed in the present paper. This effect is indeed observed in the photoemission spectra [1, 2]. For a more detailed analysis it would be important to carry out electronic structure calculations for CaVO_3 in order to study orthorhombic distortions and possible reconstructions at the surface.

In summary, we have performed DMFT quasi-particle calculations for SrVO_3 in the bulk and at the surface. As a result of the planar nature of the t_{2g} states and the surface narrowing of the local density of states on-site correlation effects are more pronounced at the surface than in the bulk, in agreement with photoemission data. The two-dimensional character of d states near E_F is one of the hallmarks of transition metal oxides. The surface-induced enhancement of correlation effects discussed in the present work should therefore be a phenomenon observable in many materials.

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